

Effects of Structure-Manipulated Molecular Stacking on the Solid-State Optical Properties and Device Performances

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1. Experimental Section

1.1. Measurements and Characterizations.

The ¹H NMR and ¹³C NMR spectra were measured on a Bruker AVANCE 400 MHz spectrometer using tetramethylsilane (TMS; δ = 0 ppm) as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III mass spectrometer. Elemental analysis was performed on a flash EA1112 analyzer. IR spectra were recorded on a TENSOR-27 spectrometer using KBr pellets. The molecular weight of the polymers was measured by gel permeation chromatograph (GPC) in THF using polystyrene as a standard. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 at a heating rate of 10 °C/min under nitrogen flow. UV-vis absorption was recorded on a Hitachi U-3010 spectrometer. The electrochemical measurements were carried out in a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in acetonitrile with a computer-controlled Zennium electrochemical workstation. A glassy carbon electrode, a Pt wire, and an Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. AFM images were obtained from the OTFT or OSC samples using a Nanoscope V AFM (Digital Instruments) in tapping mode. X-ray diffraction (XRD) samples of pristine polymer films or polymer/PCBM blending films were prepared by spin-casting of solutions on silica slides. The XRD pattern was recorded by a Rigaku D/max-2500 diffractometer operated at 40 kV voltage and a 200 mA current with Cu Kα radiation.

1.2. Fabrications and Characterizations of OTFT Devices.

An n-type heavily doped Si wafer with a SiO₂ layer of 300 nm (with a capacitance of 11 nF·cm⁻²) served as the bottom gate electrode and dielectric layer, respectively. The bottom Au contacts were prepared by photolithography and the device channel lengths, defined as the distance between source and drain was 5 μm. The channel width was 1400 μm. Before deposition of the organic semiconductor, the gate dielectrics were treated with octadecyltrichlorosilane (OTS) in a vacuum oven at a temperature of 120 °C, forming an OTS self-assembled monolayer. The treated substrates were rinsed successively with heptane, ethanol, and chloroform. A polymer layer was deposited on the OTS-treated Si/SiO₂ substrates by spin-coating of a chlorobenzene (CB) solution (10 mg/ml). The resulting thin films were annealed at 80 °C for 60 minutes in vacuum to dry the solvent and improve the film quality and morphology. The field-effect mobility was calculated in the saturation region using the following equation: $I_{ds} = (WC_i/2L)\mu(V_G - V_T)^2$, where I_{ds} is the drain-source current, W and L are the channel width (1400 μm) and length (5 μm), respectively, μ is the field-effect mobility, C_i is the capacitance per unit area of the insulation layer (SiO₂, 11 nF·cm⁻²), V_T and V_G are the gate and threshold voltages, respectively.

1.3. Fabrications and Characterizations of Polymer Solar Cells.

The OPV devices were fabricated with configurations of ITO/PEDOT:PSS/Polymer/PCBM/Ca/Al. The indium tin oxide (ITO) glass was precleaned, respectively, with deionized water, acetone and isopropanol and treated in an Novascan PSD-ultraviolet-ozone chamber for 30 min. A thin layer (ca. 30 nm) of poly(3,4-ethylene-dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P VP AI 4083, Germany) was spin-coated onto the ITO glass with spin-coating speed of 2000 rpm and baked at 150 °C for 10 min. A 1,2-dichlorobenzene solution of polymer/PCBM (30 mg/mL) subsequently spin-coated on the surface of the PEDOT:PSS layer to form a photosensitive layer (ca. 100 nm). Then, the Ca/Al cathode was deposited on the photoactive layer by vacuum evaporation (ca. 20/80 nm). The effective area of one cell is 6 mm². The current-voltage (I-V) measurement of the devices was conducted on a computer-controlled Keithley 2400 Source Measure Unit. A xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample was 100 mW/cm². IQE and EQE measurements were carried out on an oriel IQE 200 (Newport).

1.4. Tests of the hole mobilities of blending films for PTPD-T/PC71BM and PTPD-Se/PC71BM.

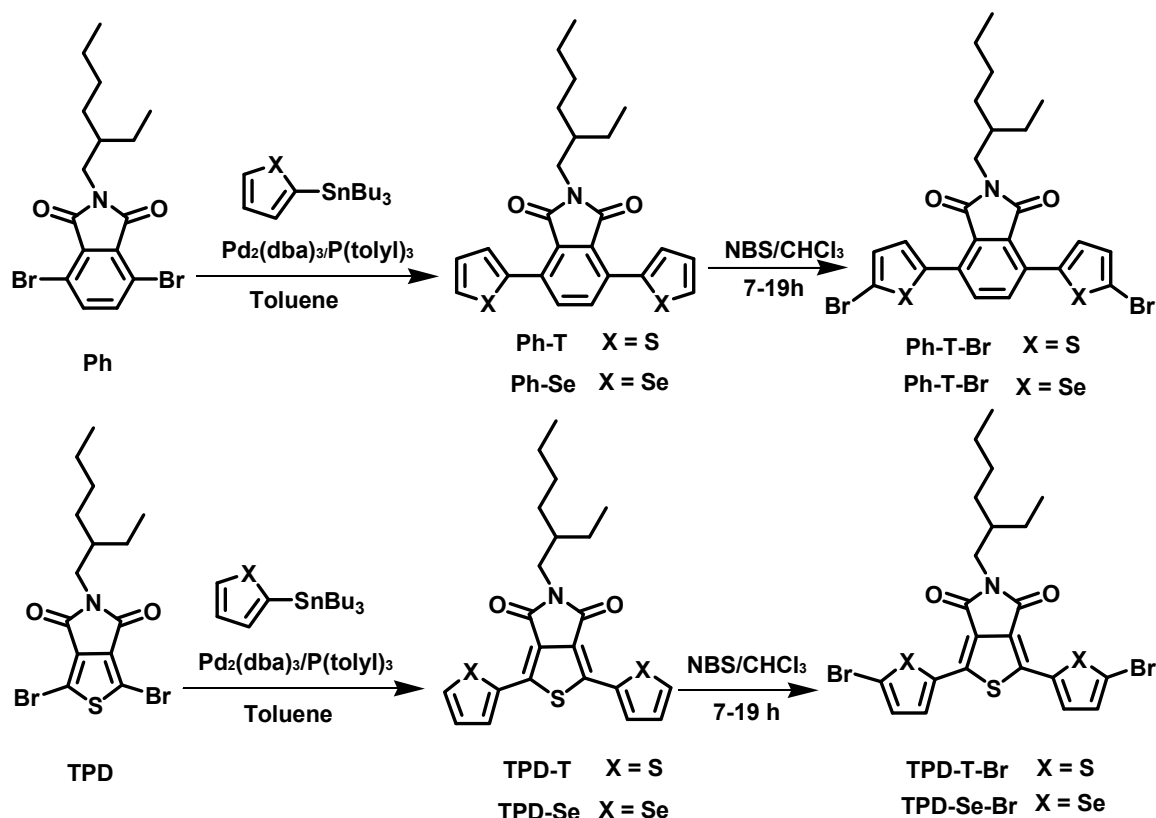
The devices were fabricated with configuration of ITO/PEDOT:PSS/PTPD-T or PTPD-Se: PC₆₁BM/Au. The active layers were spin-coated under the conditions that afford the best photovoltaic results. The following

equation was applied to estimate the hole mobilities:^{1,2} $\ln(JL^3V^2) = 0.89(1/E_0)^{0.5}(V/L)^{0.5} + \ln(9\epsilon\epsilon_0\mu_0/8)$, where ϵ is the dielectric constant of the polymer, ϵ_0 the permittivity of the vacuum, μ_0 the zero-field mobility, E_0 the characteristic field, J the current density, L the thickness of the films, and $V = V_{\text{appl}} - V_{\text{bi}}$; V_{appl} is the applied potential, and V_{bi} the built-in potential which results from the difference in the work function of the anode and the cathode (in this device structure, $V_{\text{bi}} = 0.2$ V). The $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$ plots of the small molecules based on SCLC method is shown in Figure S4. The hole mobility of the blending films were deduced from the intercept value $\ln(9\epsilon\epsilon_0\mu_0/8)$. Herein ϵ is 3, ϵ_0 is 8.85419×10^{-12} $\text{CV}^{-1}\text{m}^{-1}$.

1.5. Materials.

All of the starting materials and solvents were purchased from Sigma Aldrich or Alfa Aesar and were used without further purification, unless otherwise stated. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl under nitrogen before use. 5,5'-bis(tributylstannyl)-3,3'-didodecyl-2,2'-bithiophene (BT-(SnMe₃)₂) were synthesized according to the literature methods.^{3,4} Synthetic details of 4,7-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)isoindoline-1,3-dione (PhI-T-Br), 4,7-bis(5-bromoselenophen-2-yl)-2-(2-ethylhexyl) isoindoline-1,3-dione (PhI-Se-Br), 1,3-bis(5-bromothiophen-2-yl)-5-(2-ethylhexyl)thieno[3,4-c]pyrrole-4,6-dione (TPD-T-Br), and 1,3-bis(5-bromoselenophen-2-yl)-5-(2-ethylhexyl)-thieno [3,4-c]pyrrole-4,6-dione (TPD-Se-Br) are described as follows.

1.6. Synthetic routes toward the Ph-X-Br and TPD-X-Br (X= S or Se).



Scheme S1. Synthetic routes to the acceptor units.

A typical procedure toward the Ph-X and TPD-X (X= S or Se) was as follows.

Ph⁵ (or TPD⁶), tributyl(thiophen-2-yl)stannane (or tributyl(selenophen-2-yl)stannane)⁷, and tri(o-tolyl)phosphine were dissolved in dry toluene and degassed with N₂ for 10 min. Then, tris(dibenzylideneacetone)dipalladium was added. The mixture was stirred at 120°C over night under the N₂ atmosphere. After cooling down to room temperature, toluene was then evaporated using a rotary evaporator.

The residue was purified by column chromatography on silica gel (petrol ether/dichloromethane=3:1) to give Ph-X or TPD-X (X= S or Se) as yellow solid.

Ph-T. (yield 92%). ¹HNMR (400MHz, CDCl₃): 7.77 (d, 4H), 7.48 (t, 2H), 7.18 (quartet, 2H), 3.56 (d, 2H), 1.85 (m, 1H), 1.29 (m, 8H), 0.87 (m, 6H). ¹³C NMR (100MHz, CDCl₃): 167.66, 137.44, 135.94, 132.40, 130.15, 128.11, 127.88, 127.67, 42.34, 38.31, 30.75, 28.71, 24.06, 23.18, 14.20, 10.60. MS (MALDI-TOF): calculated for C₂₄H₂₅NO₂S₂, 423.59; found *m/z* 424.01 (M⁺).

Ph-Se (yield 87%). ¹HNMR (400MHz, CDCl₃): 8.18 (d, 2H), 7.87 (d, 2H), 7.74 (s, 2H), 7.41 (t, 2H), 3.56 (d, 2H), 1.83 (m, 1H), 1.31 (m, 8H), 0.89 (m, 6H). ¹³C NMR (100MHz, CDCl₃): 167.83, 142.94, 136.23, 134.50, 133.92, 132.19, 130.18, 127.37, 42.31, 38.28, 30.71, 28.67, 24.04, 23.20, 17.44, 14.22, 13.75, 10.60. MS (MALDI-TOF): calculated for C₂₄H₂₅NO₂Se₂, 517.38; found *m/z* 517.90 (M).

TPD-T. (yield, 88%). ¹HNMR (400MHz, CDCl₃): 8.03 (d, 2H), 7.44 (d, 2H), 7.13 (t, 2H), 3.57 (d, 2H), 1.85 (m, 1H), 1.33 (m, 8H), 0.90 (m, 6H). ¹³C NMR (100MHz, CDCl₃): 163.00, 136.57, 132.60, 130.05, 128.72, 128.57, 42.63, 38.41, 30.76, 28.75, 24.06, 23.19, 14.24, 10.62. MS (MALDI-TOF): calculated for C₂₂H₂₃NO₂S₃, 429.62; found *m/z* 428.90 (M).

TPD-Se. (yield, 80%). ¹HNMR (400MHz, CDCl₃): 8.21 (d, 2H), 7.95 (d, 2H), 7.34 (t, 2H), 3.57 (d, 2H), 1.86 (m, 1H), 1.33 (m, 8H), 0.90 (m, 6H). ¹³C NMR (100MHz, CDCl₃): 163.23, 139.09, 136.68, 135.85, 131.84, 130.45, 127.96, 42.67, 38.33, 30.69, 28.67, 24.02, 23.21, 14.23, 10.61. MS (MALDI-TOF): calculated for C₂₂H₂₃NO₂Se₃, 523.41; found *m/z* 524.90 (M⁺).

A typical procedure toward the Ph-X-Br and TPD-X-Br (X= S or Se) was as follows.

N-bromosuccinimide (NBS, 2.5 eq.) was added in one portion to a chloroform solution of Ph-X or TPD-X (X= S or Se). The mixture was stirred at room temperature under the N₂ atmosphere for 7~19 h, monitored by TLC until the reactant converted completely. It was then washed with water and the organic layer was dried over magnesium sulfate and filtered. After removing the organic solvent, the crude product was purified by column chromatography on silica gel (petrol ether/dichloromethane=4:1).

Ph-T-Br. (yield, 95%). ¹HNMR (400MHz, CDCl₃): 7.69 (s, 2H), 7.51 (d, 2H), 7.12 (d, 2H), 3.56 (d, 2H), 1.82 (m, 1H), 1.29 (m, 8H), 0.89 (m, 6H). ¹³C NMR (100MHz, CDCl₃): 167.46, 138.66, 135.45, 131.58, 130.72, 130.51, 127.99, 115.20, 42.42, 38.33, 30.73, 28.73, 24.05, 23.17, 14.20, 10.58. MS (MALDI-TOF): calculated for C₂₄H₂₃Br₂NO₂S₂, 581.38; found *m/z* 581.80 (M).

Ph-Se-Br. (yield, 93%). ¹HNMR (400MHz, CDCl₃): 7.73 (s, 2H), 7.58 (d, 2H), 7.33 (d, 2H), 3.57 (d, 2H), 1.83 (m, 1H), 1.29 (m, 8H), 0.89 (m, 6H). ¹³C NMR (100MHz, CDCl₃): 167.95, 143.98, 134.99, 133.65, 133.27, 131.88, 126.85, 120.50, 42.38, 38.31, 30.69, 28.64, 24.02, 23.19, 14.22, 10.58. MS (MALDI-TOF): calculated for C₂₄H₂₃Br₂NO₂Se₂, 675.17; found *m/z* 675.70 (M).

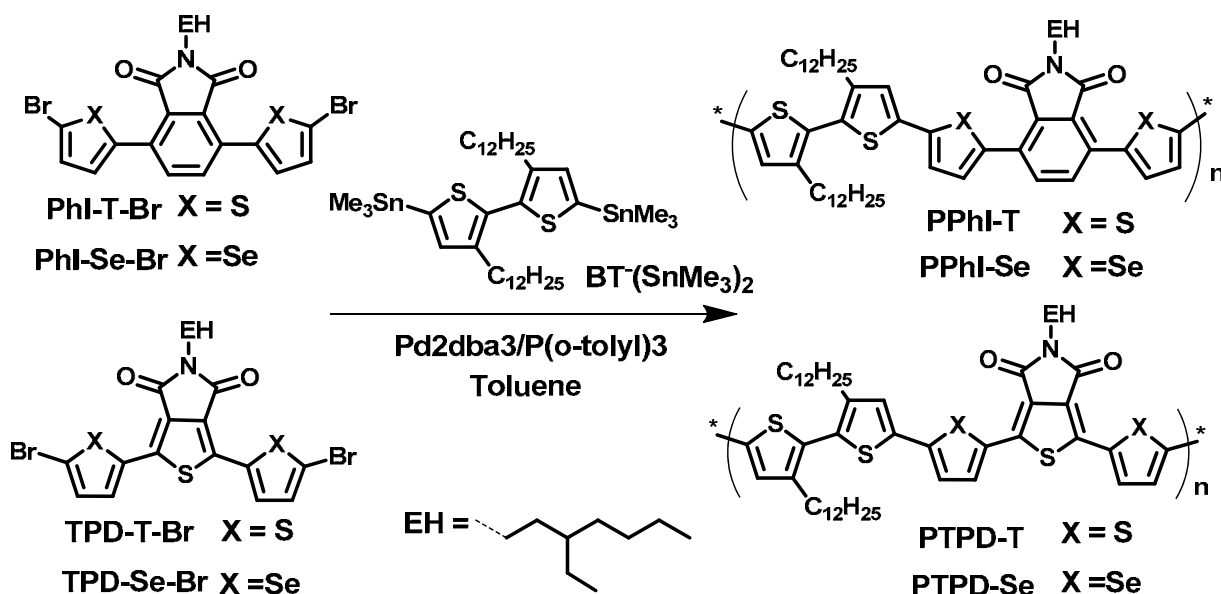
TPD-T-Br. (yield, 90%). ¹HNMR (400MHz, CDCl₃): 7.66 (d, 2H), 7.07 (d, 2H), 3.55 (d, 2H), 1.82 (m, 1H), 1.31 (m, 8H), 0.89 (m, 6H). ¹³C NMR (100MHz, CDCl₃): 162.71, 135.18, 133.87, 131.27, 129.91, 128.67, 116.89, 42.72, 38.25, 30.75, 28.73, 24.06, 23.19, 14.24, 10.60. MS (MALDI-TOF): calculated for C₂₂H₂₁Br₂NO₂S₃, 587.41; found *m/z* 586.80 (M).

TPD-Se-Br. (yield, 89%). ¹HNMR (400MHz, CDCl₃): 7.48 (d, 2H), 7.24 (d, 2H), 1.81 (m, 1H), 1.29 (m, 8H), 0.89 (m, 6H). ¹³C NMR (100MHz, CDCl₃): 162.97, 138.27, 137.77, 133.53, 130.92, 128.00, 122.76, 42.63, 38.39, 30.70, 28.65, 24.04, 23.21, 14.25, 10.59. MS (MALDI-TOF): calculated for C₂₂H₂₁Br₂NO₂Se₃, 681.20; found *m/z* 680.70 (M).

1.7. Polymer Synthesis

The four copolymers, **PPhI-T**, **PPhI-Se**, **PTPD-T**, and **PTPD-Se** were synthesized by stille coupling reaction (Scheme 2). A typical procedure toward the four copolymers was as follows. The dibrominated monomer of PhI-T(Se)-Br or TPD-T(Se)-Br (0.18 mmol), distannyl monomer BT-(SnMe₃)₂ (0.18 mmol), and tri(*o*-tolyl)phosphine (16 mol%) were dissolved in dry toluene and degassed with N₂ for 10 min.

Tris(dibenzylideneacetone)dipalladium (3 mol%) was added and the solution was degassed with N₂ for another 10 min. The mixture was heated at 120 °C for 48 h under the N₂ atmosphere. 2-tributylstannylthiophene and 2-bromothiophene were added individually to the reaction solution to end-cap the copolymer. After cooling to room temperature, the solution was added dropwise into methanol. The precipitates were filtered and collected. The collected solid was then washed successively with acetone, hexane, and chloroform in Soxhlet apparatus, respectively. The final chloroform fraction was concentrated to 10 mL and then added dropwise to methanol (100 mL) and the precipitates were collected and dried under vacuum to afford the desired copolymers.



Scheme S2. Synthetic routes toward the four copolymers.

PPhI-T was obtained as red solid (80 mg, 48%). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.79 (s, 2H), 7.31 (s, 2H), 7.23 (s, 2H), 7.15 (s, 2H), 3.61 (br, 2H), 2.56 (s, 4H), 1.87 (br, 1H), 1.26 (br, 48H), 0.88 (br, 12H). Anal. calcd for (C₅₆H₇₇NO₂S₄)_n: C, 72.75%, H, 8.40%, N, 1.52%. Found: C, 73.80%, H, 7.92%, N, 1.24%. IR (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 2960.92, 2924.36, and 2852.51 (C-H), 1704.09 (C=O), 1602.02 (phenyl), 1020.28 (C-S). GPC (THF): Mn, 15.0 kg/mol, Mw/Mn=2.1.

PPhI-Se was obtained as a red solid (143 mg, 78%). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.85 (br, 2H), 7.78 (br, 2H), 7.36 (br, 2H), 7.01 (br, 2H), 3.55 (br, 2H), 2.54 (br, 4H), 1.67 (br, 1H), 1.24 (br, 48H), 0.87 (br, 12H). Anal. calcd for (C₅₆H₇₇NO₂S₂Se₂)_n: C, 66.05%, H, 7.62%, N, 1.38%. Found: C, 67.35%, H, 7.02%, N, 1.33%. IR (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 2961.73, 2922.71, and 2851.86 (C-H), 1697.82 (C=O), 1542.17 (phenyl), 1093.47 and 1023.11 (C-S). GPC (THF): Mn, 14.1 kg/mol, Mw/Mn=4.8.

PTPD-T was obtained as a black-purple solid (107 mg, 64%). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.50–7.77 (br, 2H), 7.12 (br, 2H), 6.99 (br, 2H), 3.57 (br, 2H), 2.51 (br, 4H), 1.88 (br, 1H), 1.24 (br, 48H), 0.86 (br, 12H). Anal. calcd for (C₅₄H₇₅NO₂S₅)_n: C, 69.70%, H, 8.12%, N, 1.51%. Found: C, 69.52%, H, 8.33%, N, 1.46%. IR (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 2957.39, 2922.42, and 2851.77 (C-H), 1694.65 (C=O), 1088.60, 1056.96, and 1015.41 (C-S). GPC (THF): Mn, 10.0 kg/mol, Mw/Mn=2.3.

PTPD-Se was obtained as a black-purple solid (110 mg, 60%). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.7 (br, 2H), 7.52 (br, 2H), 7.05–7.15 (br, 2H), 3.57 (br, 2H), 2.47–2.52 (br, 4H), 1.88 (br, 1H), 1.25 (br, 48H), 0.87 (br, 12H). Anal. calcd for (C₅₄H₇₅NO₂S₃Se₂)_n: C, 63.32%, H, 7.38%, N, 1.37%. Found: C, 64.33%, H, 7.15%, N, 1.30%. IR (KBr), $\nu_{\text{max}}/\text{cm}^{-1}$: 2957.38, 2922.90, and 2852.12 (C-H), 1691.86 (C=O), 1086.88 (C-S). GPC (THF): Mn, 12.5 kg/mol, Mw/Mn=3.2.

2. Supporting figures.

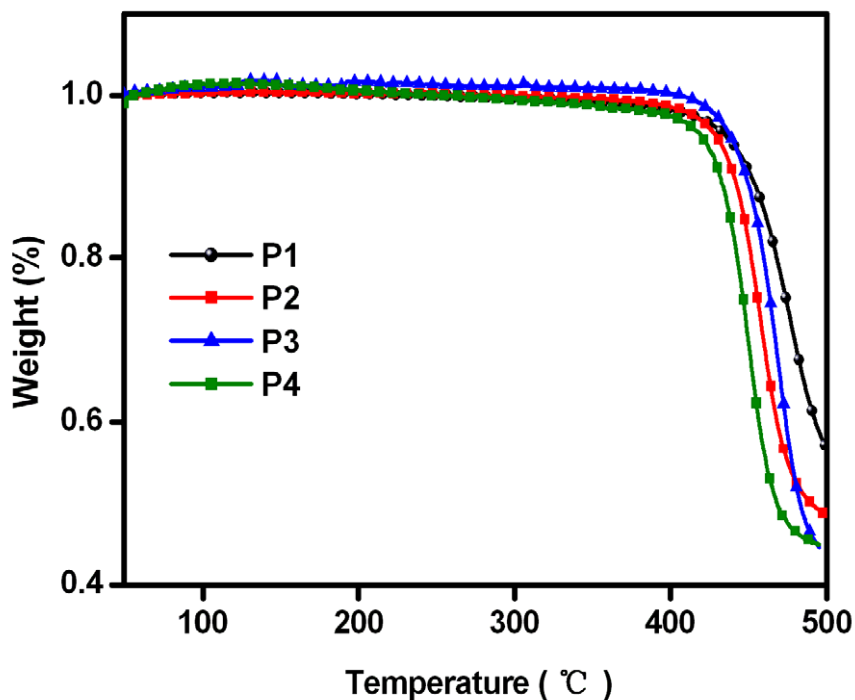


Figure S1. TGA curves of the copolymers of P1, P2, P3, and P4.

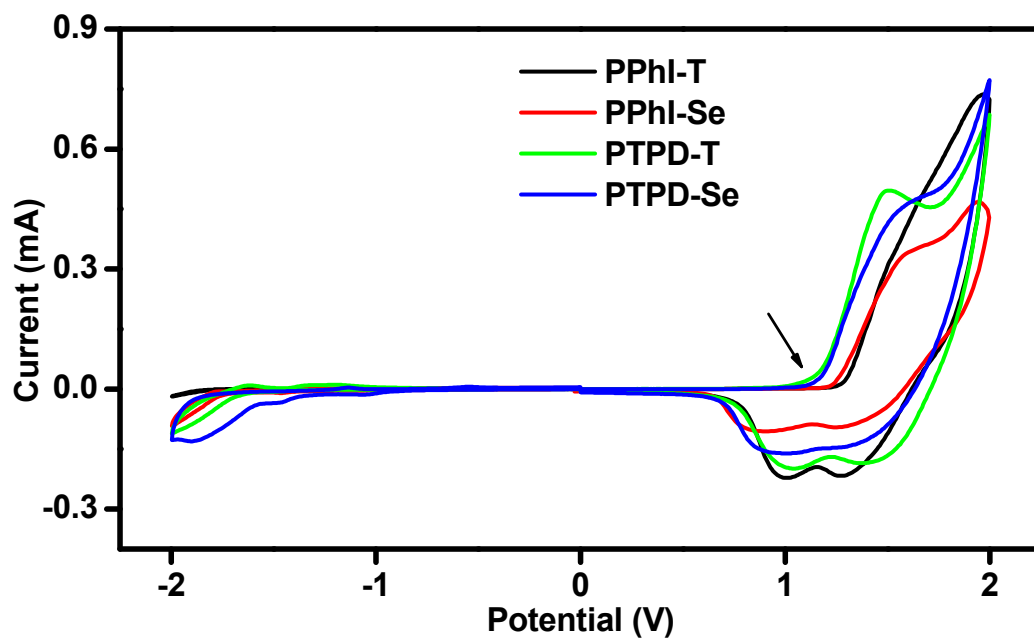


Figure S2. (a) Cyclic voltammograms of synthesized polymeric films in $\text{CH}_3\text{CN}/0.1 \text{ M } [\text{nBu}_4\text{N}]^+[\text{PF}_6]^-$ at 100 mV/s .

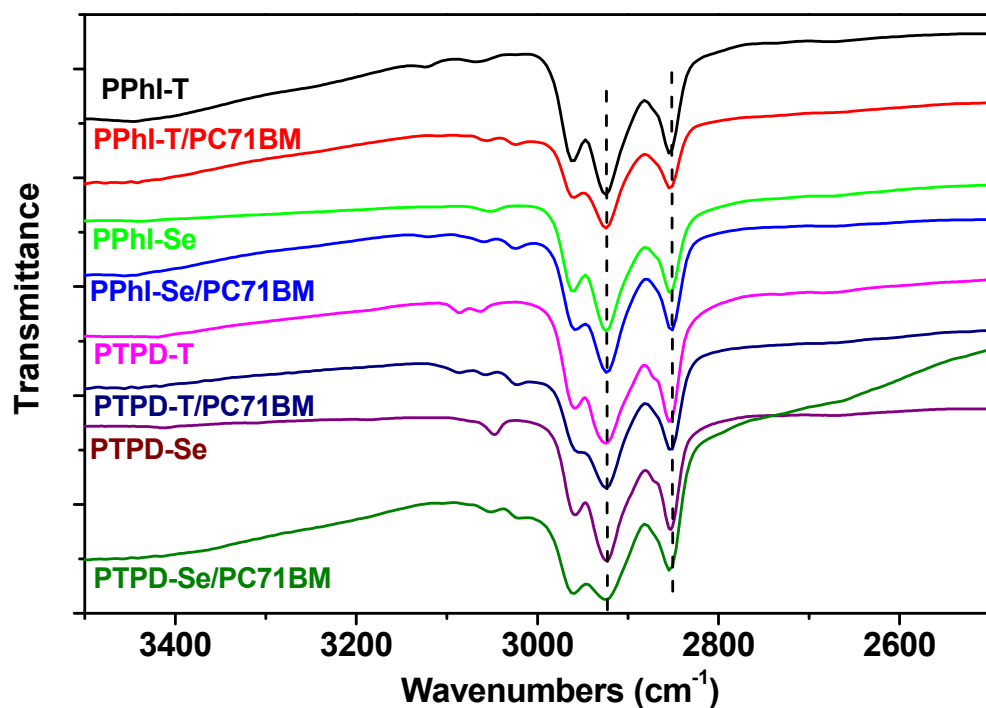


Figure S3. The CH₂ symmetric and antisymmetric stretching bands in pristine polymer films and polymer/PC71BM blending films.

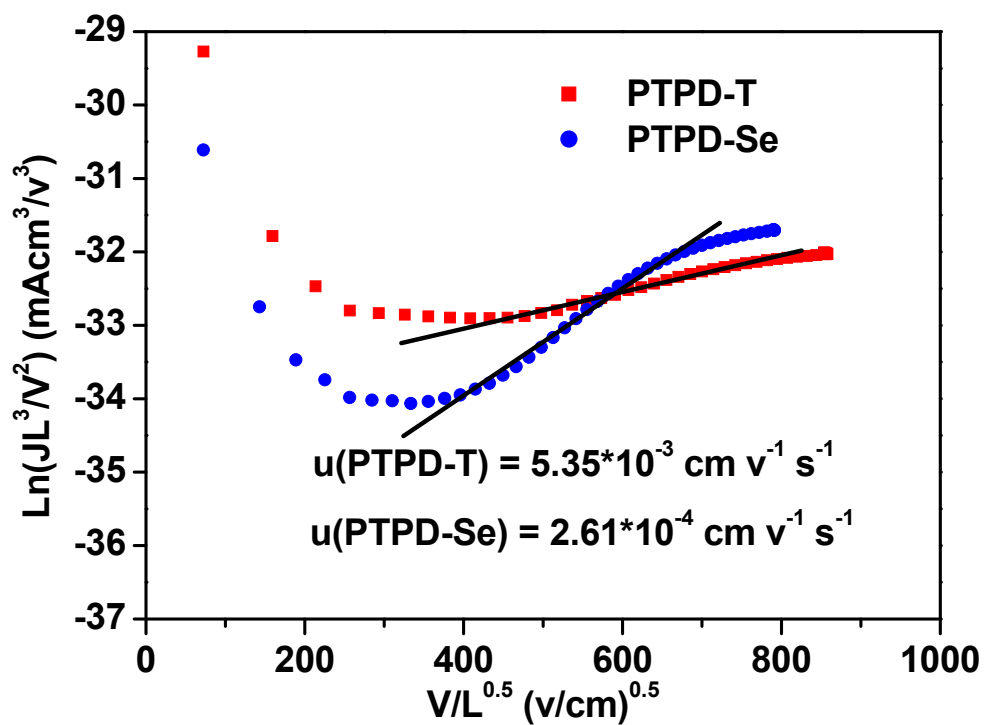


Figure S4. Plots of $\ln(JL^3/V^2)$ vs. $(V/L)^{0.5}$ of the small molecules.

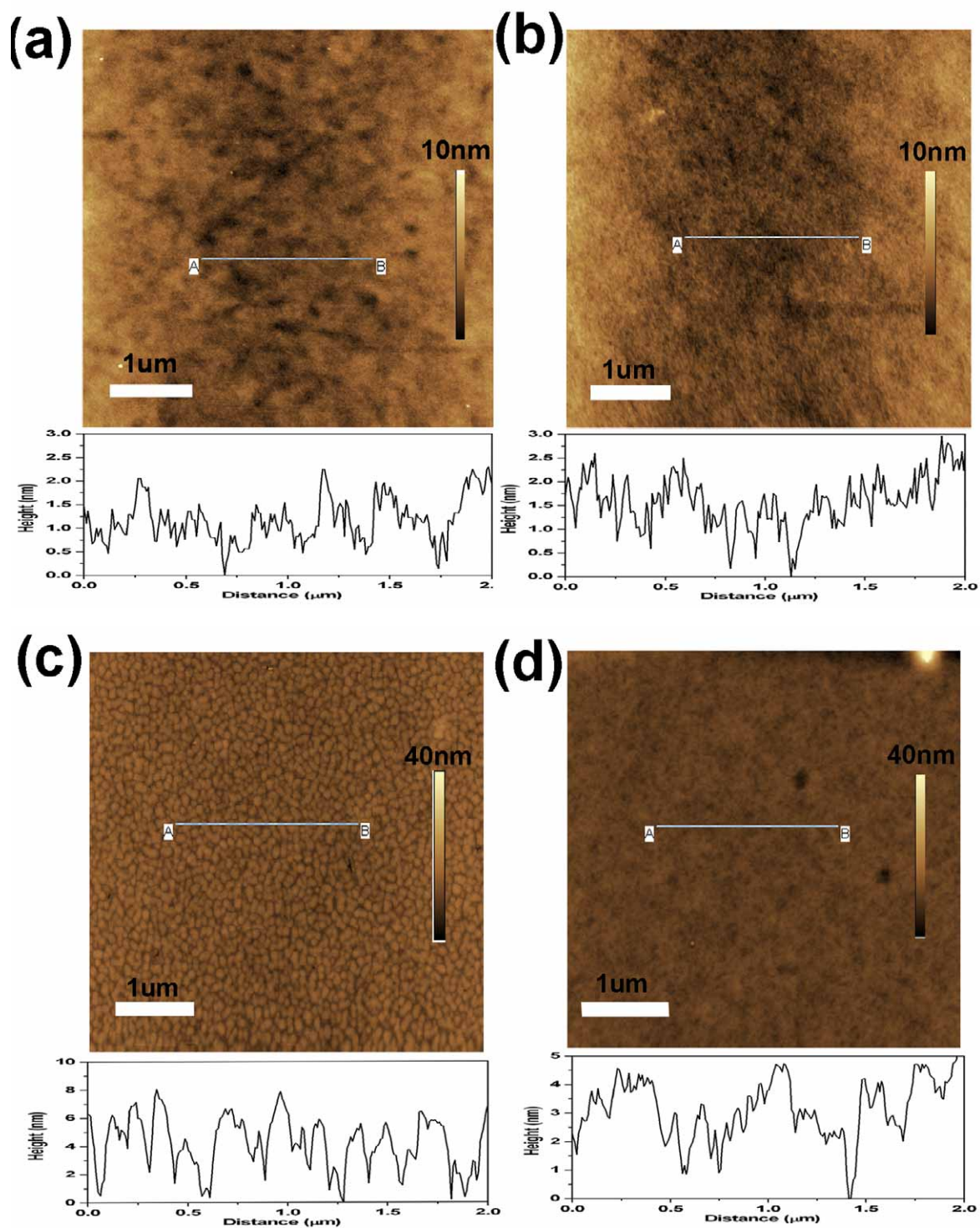


Figure S5. Tapping mode AFM images of PPhI-T/PC61BM (a), PPhI-Se/PC61BM (b), PTPD-T/PC61BM (c), and PTPD-Se/PC61BM (d). Note: scan area: $5 \times 5 \mu\text{m}$, R_q roughness = 1.09 nm (a), 1.23 nm (b), 1.96 nm (c), 1.56 nm (d).

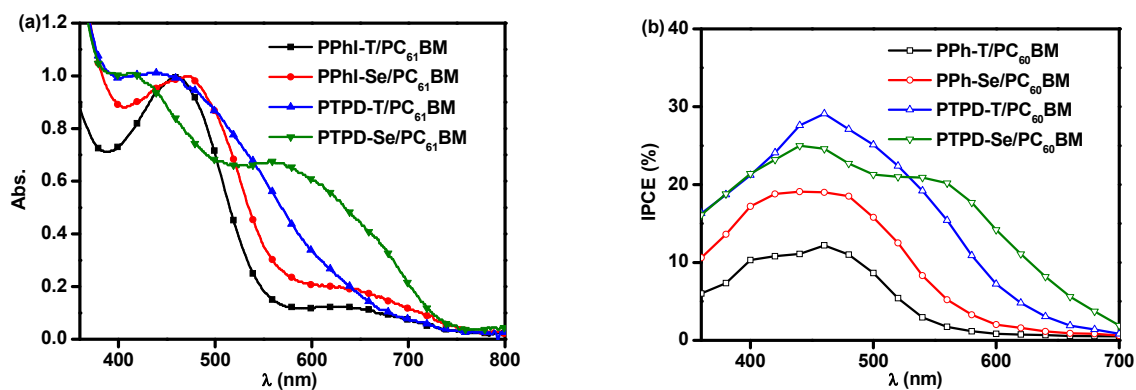


Figure S6. Absorption spectrum of the polymer/PC₆₁BM blending films (a) and IPCE of the solar cells based on polymer/PC₆₁BM (b).

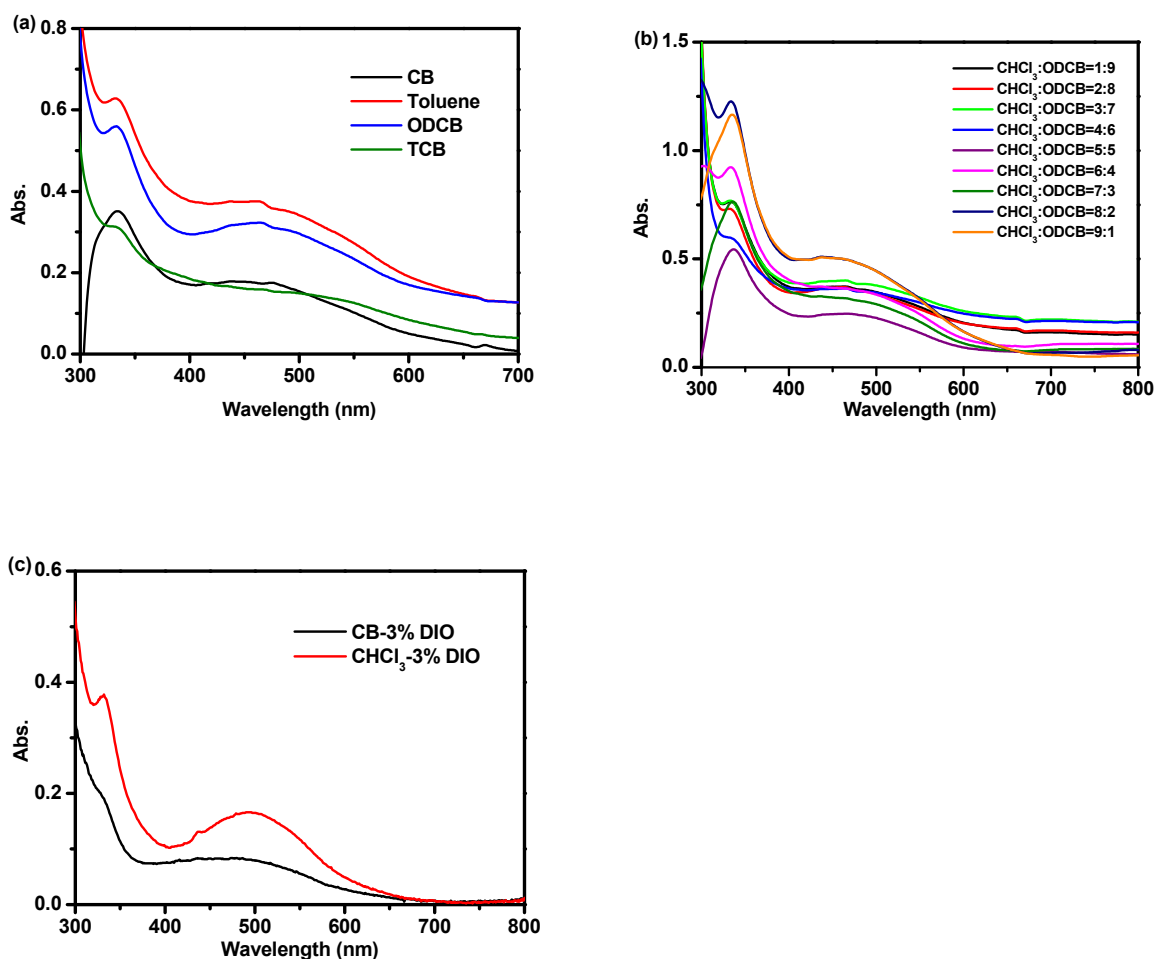


Figure S7. absorption spectrum of PTPD-T/PC₆₁BM active layers, casting from (a) different solvent of chlorobenzene (CB), Toluene, ortho dichloro benzene (ODCB), and 1,3,5-trichlorobenzene (TCB), (b) CHCl₃/ODCB blending solvent with different ratios, and (c) CB and CHCl₃ with 3% (vol) of DIO, respectively.

3. Characterization data

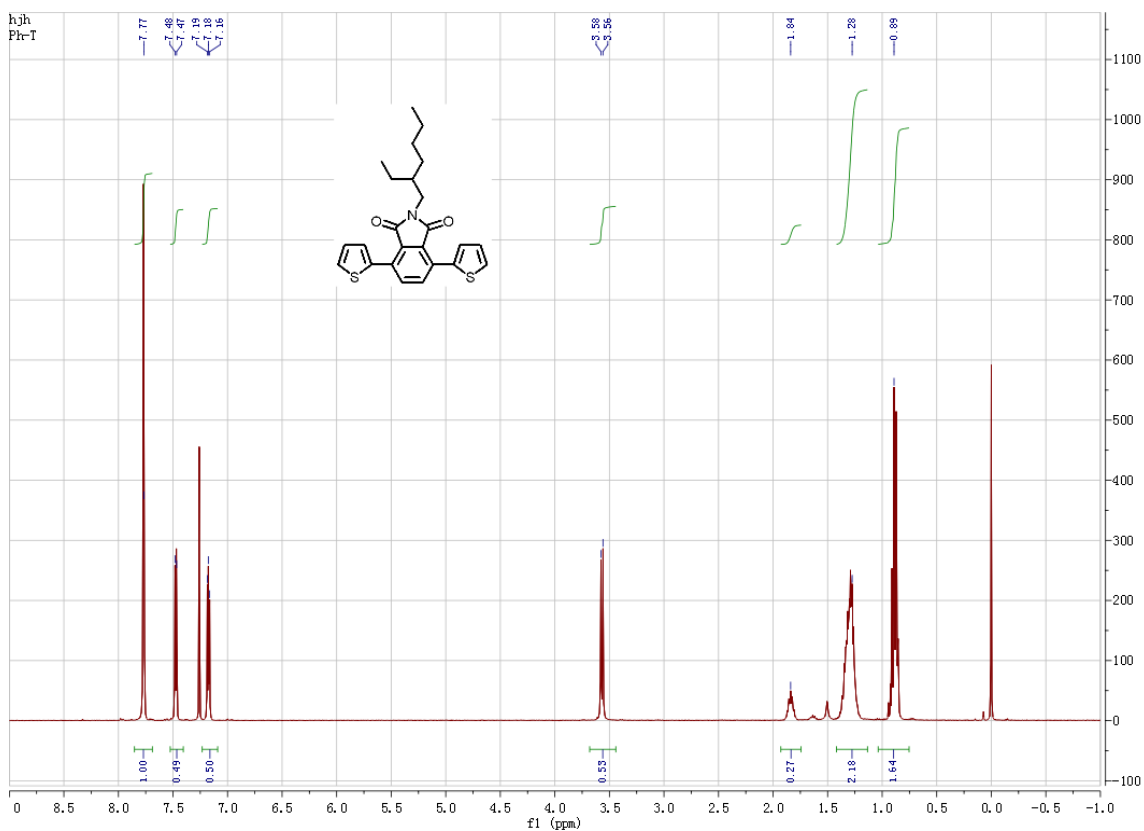


Figure S8. ^1H NMR (400MHz) of Ph-T in CDCl_3 .

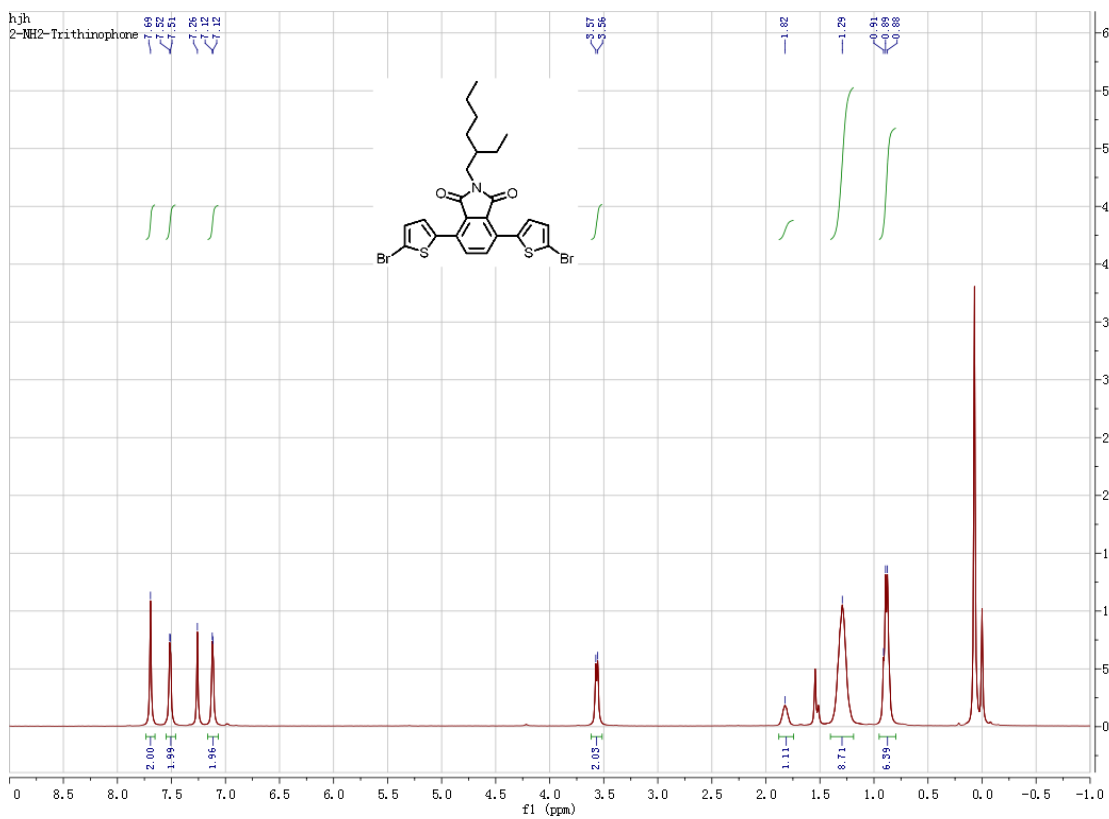


Figure S9. ^1H NMR (400MHz) of compound Ph-T-Br in CDCl_3 .

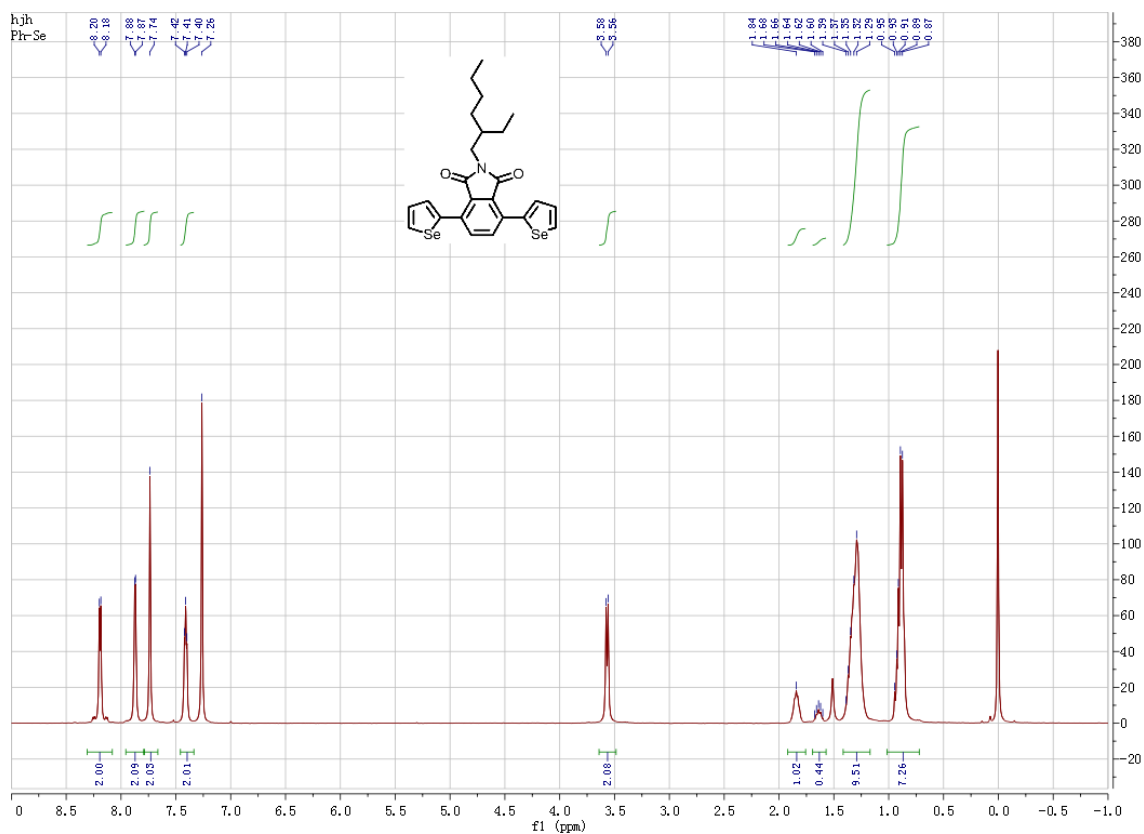


Figure S10. ^1H NMR (400MHz) of Ph-Se in CDCl_3 .

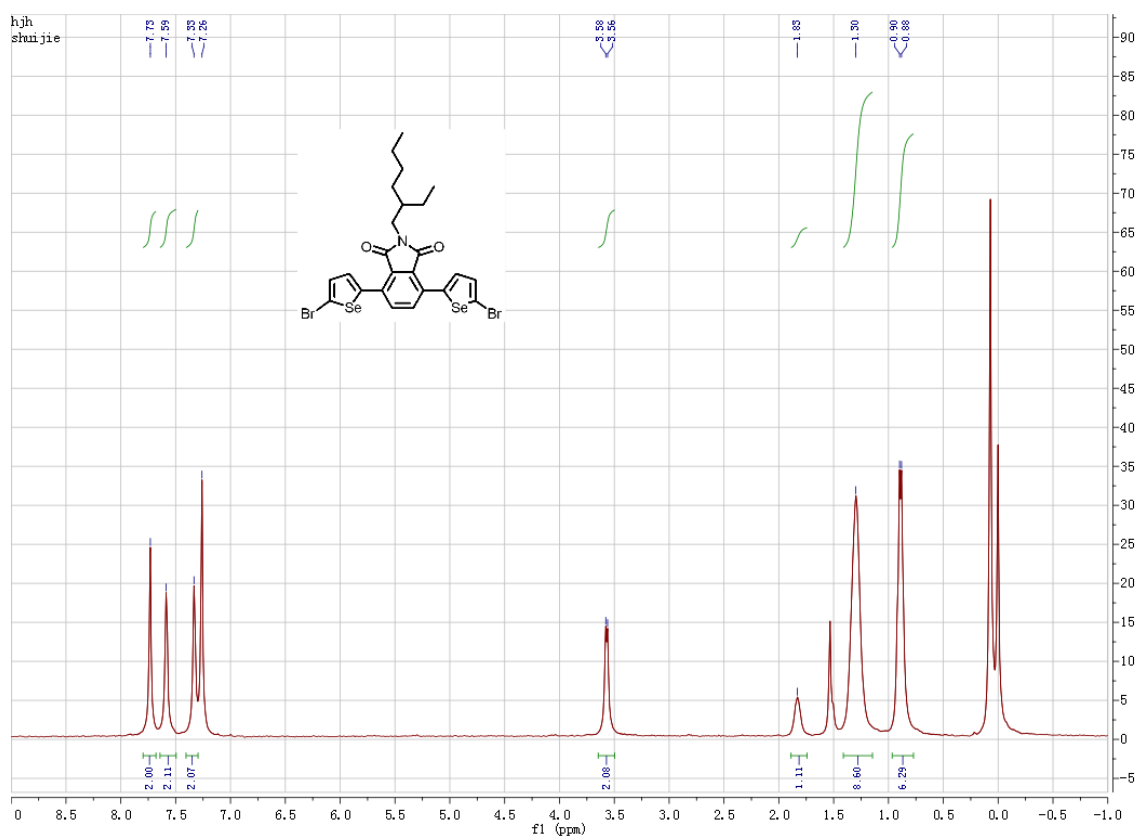


Figure S11. ^1H NMR (400MHz) of Ph-Se-Br in CDCl_3 .

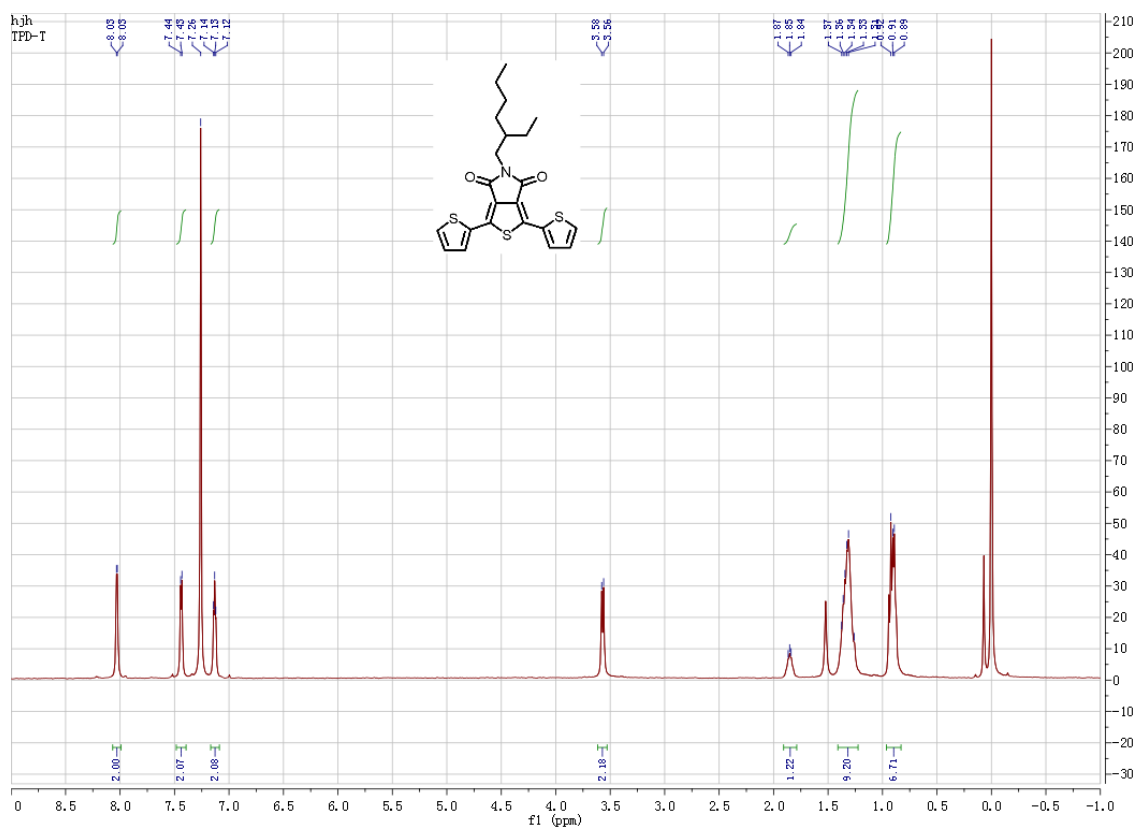


Figure S12. ^1H NMR (400MHz) of TPD-T in CDCl_3 .

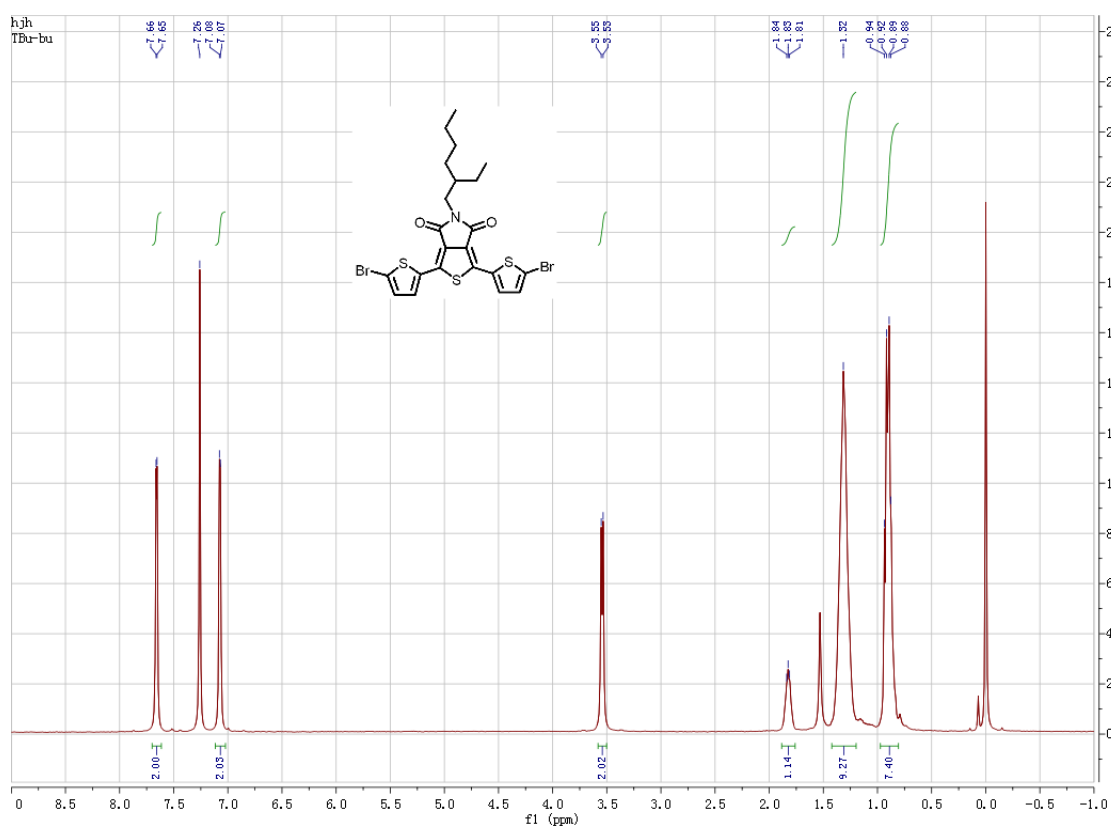


Figure S13. ^1H NMR (400MHz) of TPD-T-Br in CDCl_3 .

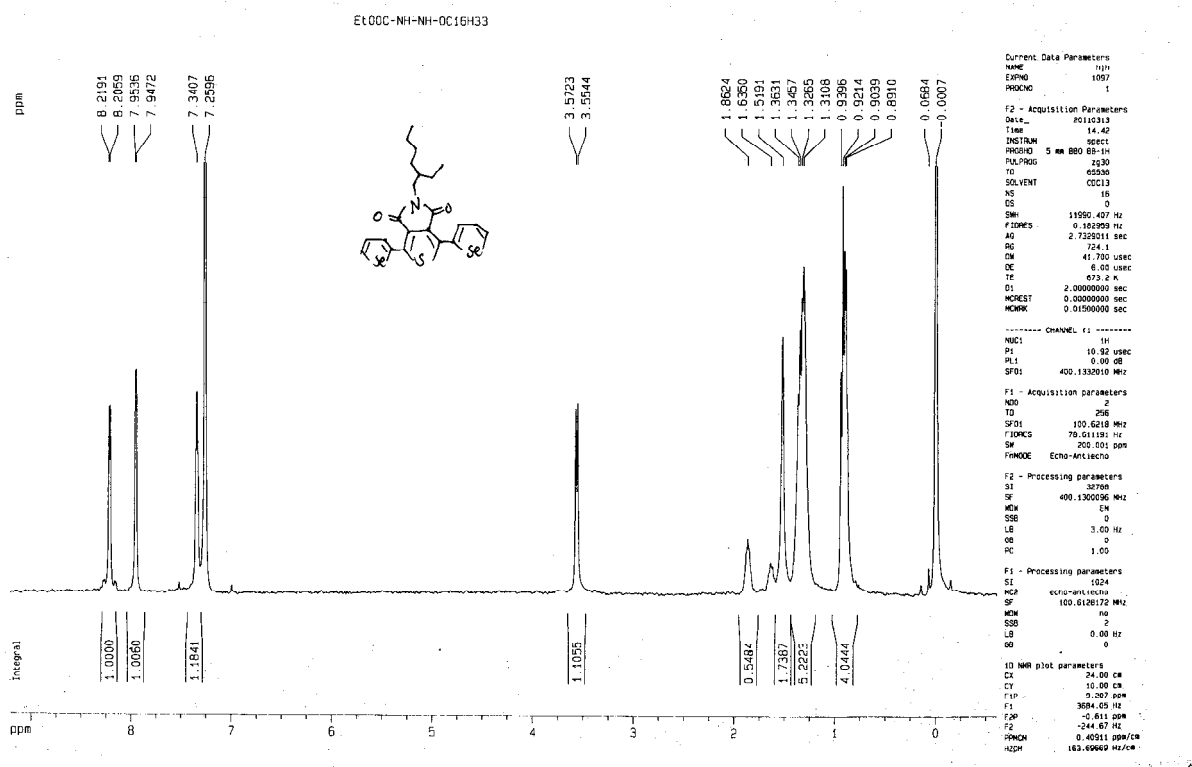


Figure S14. ¹H NMR (400MHz) of TPD-Se-Br in CDCl₃.

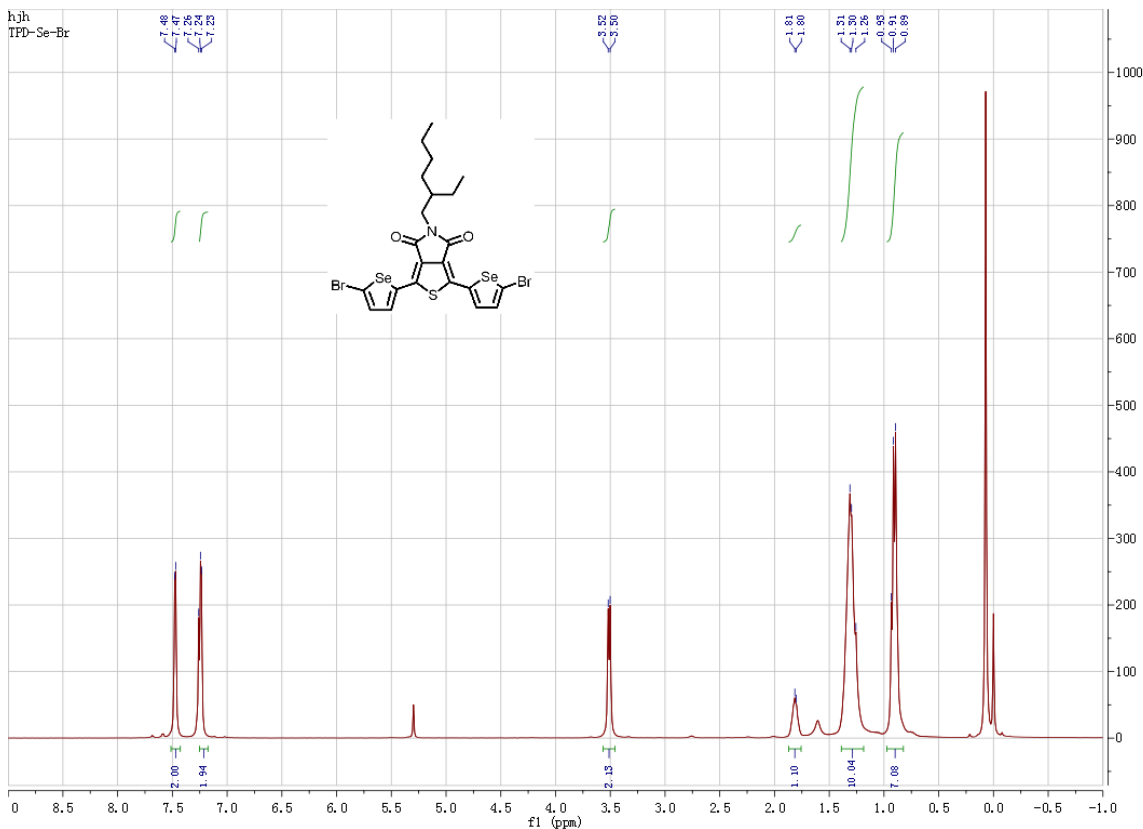


Figure S15. ¹H NMR (400MHz) of TPD-Se-Br in CDCl₃.

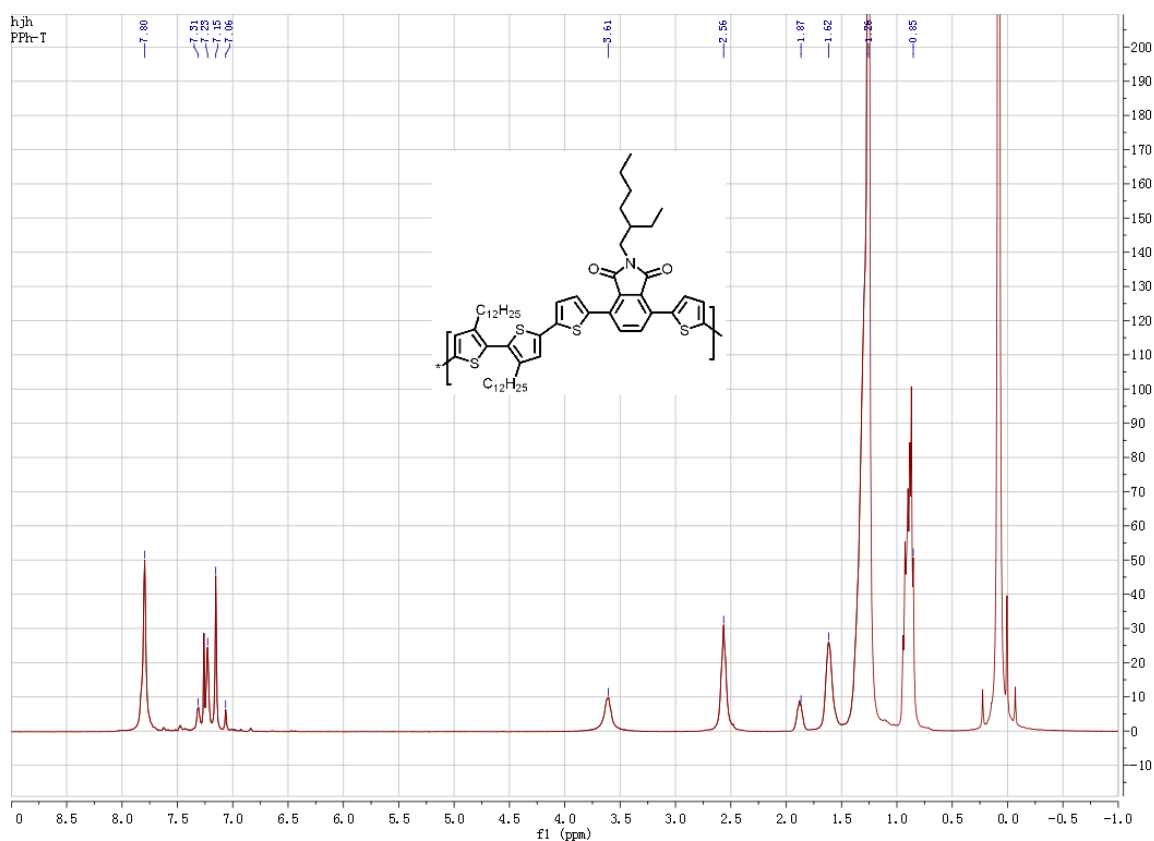


Figure S16. ^1H NMR (400MHz) of PPh-T in CDCl_3 .

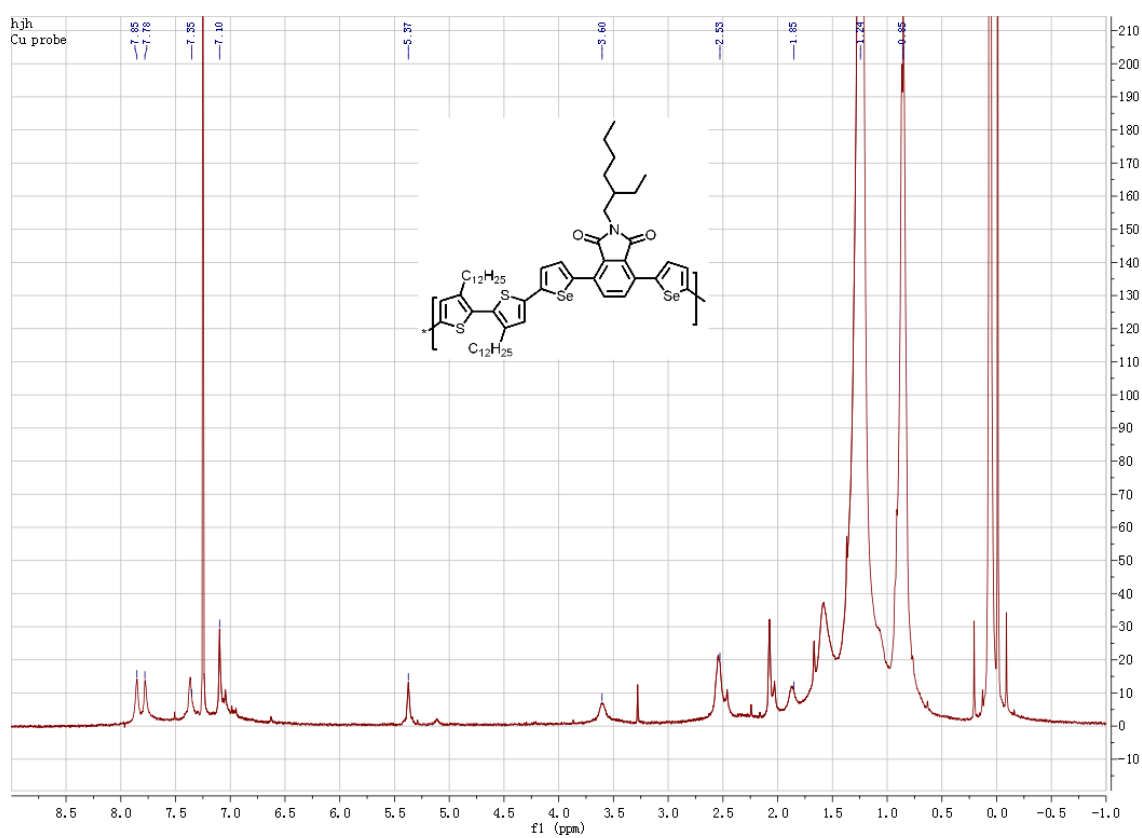


Figure S17. ^1H NMR (400MHz) of PPh-Se in CDCl_3 .

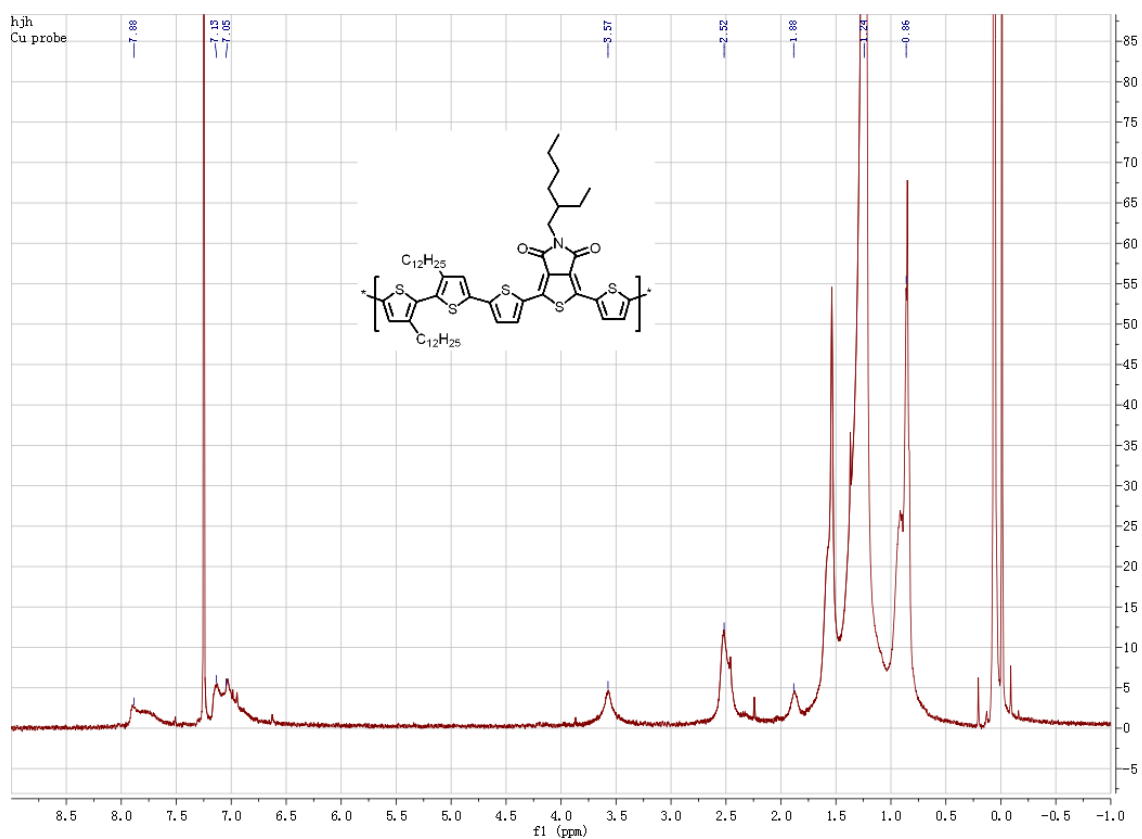


Figure S18. ^1H NMR (400MHz) of PTPD-T in CDCl_3 .

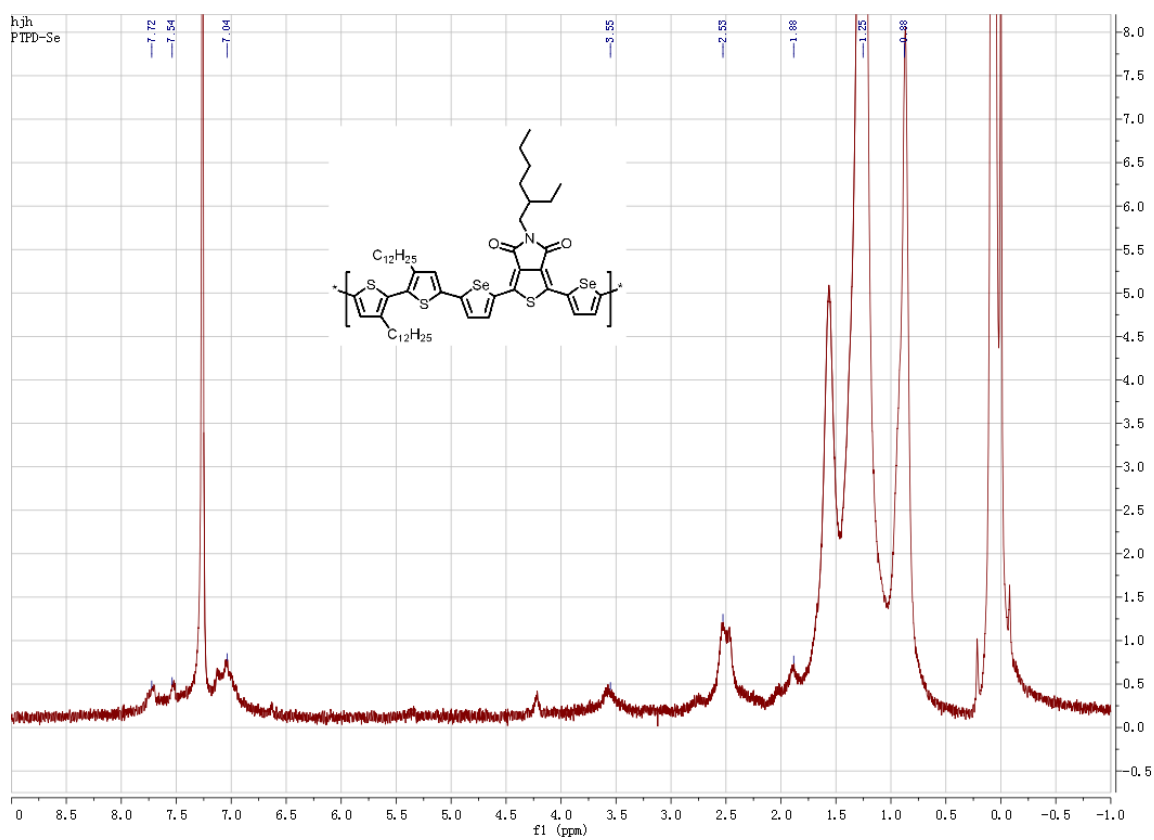


Figure S19. ^1H NMR (400MHz) of PTPD-Se in CDCl_3 .

4. References:

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